United States Patent

Lang et al.

NOVEL DIAZAMEROCYANINES AND THEIR USE FOR DYEING KERATINOUS FIBERS

Inventors: Gerard Lang, Epinay-sur-Seine; Andree Bugaut, Boulogne-sur-Seine, both of France
Assignee: Societe Anonyme dite: L'Oreal, Paris, France
Filed: June 5, 1972
Appl. No.: 259,689

Foreign Application Priority Data
June 4, 1971 France .......................... 71.63287
Jan. 6, 1972 France .......................... 72.64565

Int. Cl. ........................................ C07d 87/22
Field of Search .................................. 260/305, 244 R

References Cited
UNITED STATES PATENTS
3,043,828 7/1962 Hugnick ......................... 260/305

Primary Examiner—R. J. Gallagher
Attorney, Agent, or Firm—Cushman, Darby & Cushman

ABSTRACT
Novel diazamercyanines and salts thereof useful for dyeing keratinous fibers, particularly human hair, are disclosed. Illustrative is 3-methyl 2,3-dihydro 2,4' azino benzoiazole 3'-amino 6'-methyl 1'-oxo 1', 4'-dihydro benzene having the formula:

Hair setting lotions, hair dye compositions and hair lacquers containing the diazamercyanines, preferably in alcoholic solutions, are also disclosed.

2 Claims, No Drawings
3,869,454

NOVEL DIAZAMEROCYANINES AND THEIR USE FOR DYEING KERATINOUS FIBERS

Currently, one of the most frequently used processes in capillary dyeing includes using oxidation dyes or "bases" associated with dyeing modifiers or "couplers" which can be aromatic metadamines or metaaminophenols, or pyrazolones or diketones. When using this process of capillary dyeing, an oxidizing agent as hydrogen peroxide is added to the mixture of bases and couplers selected which has been previously alkalinized. It is known to use heterocyclic hydrazones associated with couplers for dyeing hair, as described for example in French Pat. No. 1,599,968.

However, this process has the disadvantage of requiring the use of hydrogen peroxide in an alkaline medium, which has been found to cause degradation of the hair, which rapidly becomes porous and brittle. Further, the shades obtained are capable of reproduction only with great difficulty because of secondary reactions that occur along with the reaction of coupling hydrazone and coupler. An additional disadvantage is that the hydrazones are relatively aggressive compounds in regard to the skin, which often causes problems with their use.

The present invention makes it possible to avoid these drawbacks by using, not a mixture of hydrazone and couplers thereof, but their coupling products, which constitute direct dyes which can be used over a varied range of pHs and are capable of forming easily reproducible shades. One embodiment of the present invention has as its object novel dyeing compositions for human hair, characterized by the fact that they contain in solution at least a diazamericyanine or a diazamero cyanine salt of the formula

\[ A = N - N = B \]

wherein A is a nitrogen heterocycle of the formula

wherein R is selected from the group consisting of lower alkyl having 1-4 carbon atoms and phenyl; X is selected from the group consisting of oxygen, sulfur, —NR’—, wherein R’ is lower alkyl having 1-4 carbon atoms, —CH=CH—,

\[ \text{wherein } R'' \text{ is selected from the group consisting of hydrogen and lower alkyl having 1-4 carbon atoms, and } -C(R'')(R'')- \text{, wherein } R'' \text{ each independently have the meaning given above, } Z \text{ is a member selected from the group consisting of } -CH=CH- \text{ and } -NR''- \text{, wherein } R''' \text{ is a lower alkyl having 1-4 carbon atoms; } R_1 \text{ is selected from the group consisting of hydrogen, lower alkyl having 1-4 carbon atoms and phenyl; } R_4 \text{ is selected from the group consisting of hydrogen and lower alkyl having 1-4 carbon atoms and phenyl; } R_7 \text{ and } R_8 \text{ taken together with the carbon atoms to which they are linked, form a benzene ring, a halogen-substituted benzene ring, a benzene ring substituted with lower alkyl having 1-4 carbon atoms, a benzene ring substituted with lower alkoxy having 1-4 carbon atoms or a nitro-substituted benzene ring; } B \text{ is selected from the group consisting of (i) a nitrogen-containing heterocycle different from the nitrogen containing heterocycle of } A; \text{ (ii) a cycle having the formula} \]

\[ Z \]

wherein Y is a member selected from the group consisting of oxygen and

\[ R_1 \text{ and } R_2 \text{ each independently represent a member selected from the group consisting of hydrogen, lower alkyl having 1-4 carbon atoms and phenyl; and } Z^- \text{ is an anion derived from a member selected from the group consisting of inorganic acids and organic acids, such as halide, fluoborate, perchlorate, sulfate, bisulfate and acetate; } R_3, \text{ represents a member selected from the group consisting of hydrogen, lower alkyl, lower alkoxy and phenyl carbamyl; } R_4 \text{ and } R_5 \text{ each independently represent a member selected from the group consisting of hydrogen, lower alkyl having 1-4 carbon atoms and lower alkoxy having 1-4 carbon atoms, and } R_6 \text{ represents a member selected from the group consisting of hydrogen, amino, alkylated amino having 1-4 carbon atoms, acylated amino having 2-5 carbon atoms; } R_8 \text{ and } R_{10} \text{ being able, together with the carbon atoms to which they are attached, to form a condensed benzene ring; (iii) a cycle having the formula} \]

\[ R_1 \text{ and } R_4 \text{ together with the nitrogen and carbon atoms to which they are attached, form a compound selected from the group consisting of a saturated heterocycle having 5 ring atoms, an unsaturated het-}
erocycle having 5 ring atoms, a saturated heterocycle having 6 ring atoms, an unsaturated heterocycle having 6 ring atoms, in which case $R_{1a}$ is hydrogen and $R_2$ represents a member selected from the group consisting of hydrogen and lower alkyl having 1-4 carbon atoms; or wherein $R_2$ and $R_{1b}$, when taken together with the nitrogen and carbon atoms to which they are attached, form a compound selected from the group consisting of a saturated heterocycle having 5 ring atoms, an unsaturated heterocycle having 5 ring atoms, a saturated heterocycle having 6 ring atoms and an unsaturated heterocycle having 6 ring atoms, in which case $R_2$ is hydrogen and $R_1$ is selected from the group consisting of hydrogen, lower alkyl having 1-4 carbon atoms and acyl having 2 to 5 carbon atoms; and a cycle having the formula

where $R_1$, $R_2$, $R_9$, $R_{10}$ and $R_{11}$ have the meaning given above and $X^-$ represents an anion derived from a member selected from the group consisting of inorganic acid and organic acid, such as halide, fluoroborate, perchlorate, sulfate, bisulfate and acetate.

The organic or inorganic acid salts of the compounds of Formula I can be acetates, oxalates, hydrochlorides, hydrobromides, persulfates or perchlorates. Of course, other organic and inorganic salts may be found.

Ammonia groups are compounds having the formula:

where $R_a$ and $R_b$ are each independently hydrogen and lower alkyl having 1-4 carbon atoms.

The above-described hair dyeing compositions according to the present invention are aqueous solutions, to which most often have been added low molecular weight alcohols such as ethanol or isopropanol, or glycols such as propylene glycol or butylylglycol, the alcohol or glycol facilitating the solution of the dye in the composition. These solutions are easily prepared by dissolving one or more compounds of Formula I in water or in a water-alcohol mixture. The proportion of alcohol used is generally between 20 and 70% by weight, while the proportion of glycol is generally between 1 and 6% by weight.

The concentration of the dye or dyes of Formula I in the dyeing compositions according to the present invention can vary in broad limits, because of the great affinity of these compounds for keratinous fibers. This concentration is generally between about 0.001 and about 0.5% by weight and preferably between about 0.002 and about 2% by weight.

The pH of the compositions according to the present invention is generally between about 2.5 and 10 and preferably between about 3 and 8. Preferably, however, the pH is adjusted to the desired value by addition of an acid such as orthophosphoric acid, lactic acid or acetic acid or a base such as mono-, di- or triethanolamine or ammonia.

The compositions according to the present invention can contain only one or more of the dyes of Formula I, in which case they make it possible to obtain on the hair shades rich in glints that go from yellow to blue, covering the light spectrum. The composition according to the invention can, however, contain other direct dyes, for example, azo or anthraquinone dyes, nitro dyes of the benzene series, indoanlines, indophenols or indamines.

The hair-dyeing compositions according to the present invention can also contain various auxiliaries and ingredients customarily used in capillary cosmetics, for example, wetting agents, dispersing agents, swelling agents, penetrating agents, thickeners, softeners or perfumes. They can also be packaged under pressure in aerosol bombs or containers, together with a conventional aerosol propellant such as dichlorodi-fluoromethane, trichloromono-fluoromethane and their mixtures. Of course, other conventional aerosol propellants can be used.

Dyeing of keratinous fibers, particularly human hair, with the dye compositions according to the invention, can be performed in the usual way, by application at ambient temperature of the composition to the fibers to be dyed, the composition being left in contact for a period varying from 3 to 30 minutes. Following this application, the fibers are rinsed and, if desired, washed. Thereafter the treated fibers are dried.

In another embodiment of the present invention the compounds of Formula I can be employed in the production of capillary setting lotions. These lotions comprise an aqueous dilute alcohol solution, at least one cosmetic resin and at least a compound of Formula I or a salt thereof as defined above. The setting lotions according to the invention generally contain from 20 to 70% by weight of the total hairstyling lotion composition, of a low molecular weight alkanol such as ethanol or isopropanol and from 1 to 3% by weight of cosmetic resin.

Representative cosmetic resins that can be employed in the hair-setting lotions of the present invention include, for instance, polyvinyl pyrrolidone having a molecular weight of 40,000-400,000, copolymer of crotonic acid and vinyl acetate, said copolymer having a molecular weight ranging from about 10,000 to 70,000, copolymer vinyl pyrrolidone and vinyl acetate, wherein the ratio of PVP to VA ranges between 50-70: 50-30, said copolymer having a molecular weight ranging from about 30,000 to 200,000 and maleic anhydride-butylvinyl ether copolymers, a 1% solution of which is methylethyl ketone has a viscosity of 0.1-3.5 cps at 25°C. These resins are used in a proportion of 1 to 3% by weight of the hair-setting lotion composition.

The pH of the hair setting lotions according to the invention is generally between 3 and 8. As stated above, it is possible to regulate the pH to the desired value by using mono- or di- or triethanolamine and an acidifying agents, acetic acid or lactic acid.

The setting lotions according to the invention can contain only the dyes of Formula I, in which case they constitute what is known as shading compositions. However, the hair-setting lotions of this invention can
also contain other direct dyes such as anthraquinone
dyes, nitro dyes of the benzene series and those men-
tioned above. The hair-setting lotions can also contain
various ingredients usually used in capillary cosmetics,
for example, wetting agents, dispersing agents, swelling
agents, penetrating agents, thickeners, softeners or per-
fumes, as mentioned above. The hair-setting lotions
disclosed herein are used in the customary manner by
applying at ambient temperature to wet hair that has
been previously washed and rinsed, followed by rolling
the hair up on curlers and drying of the hair.
In another embodiment of the present invention, the
dyes of Formula I can also be used in the production of
hair lacquers. These lacquers contain in alcohol solu-
tion at least one cosmetic resin and at least a compound
of Formula I.
The alcohols suitable for the preparation of the hair
lacquers according to the invention are low molecular
weight alcohols, such as ethanol or propanol. As
resins there may be used one or more of polyvinyl pyr-
rolidone, copolymer of crotonic acid and vinyl acetate,
copolymer of vinyl pyrrolidone and vinyl acetate, co-
polymer of maleic anhydride and butylvinyl ether, all
as described above. The amount of dye of Formula I
ranges from about 0.001 to about 0.5% by weight and
the amount of cosmetic resin used is between about 1
and 3% by weight. Of course the hair lacquers of the
present invention are conveniently packaged in pres-
surized containers or aerosol bombs of the type de-
scribed above. The hair lacquers are conveniently ap-
plicated directly to the hair, preferably in the form of a
spray at ambient temperature.

Of the dyes of Formula I as described above, there
are a certain number of novel compounds which are
also part of and comprise another embodiment of the
present invention.
Thus, the present invention in the composition of
matter aspect thereof, includes novel diazamercocya-
nines and salts thereof of the formula

\[ A = N - N = B' \]

wherein

A is a nitrogen heterocycle as defined above and B' is
a residue corresponding to one of the following
formulae:

\[ \text{Diagram} \]

In the above formulae X represents an anion de-
\[ \text{Diagram} \]

wherein W is selected from the group consisting of oxy-
gen and sulfur, and R is selected from the group con-
sisting of amino and lower alkyl of 1-4 carbon atoms,
R3 and R4 each independently represent a member selected from the group consisting of hydrogen and lower alkyl having 1-4 carbon atoms;
Y represents a member selected from the group consisting of

\[ \text{Diagram} \]

wherein \( R_1 \) and \( R'_2 \) each independently represent a member selected from the group consisting of hydrogen and lower alkyl having 1-4 carbon atoms, and \( Z^- \) is an anion derived from an inorganic or organic acid, such as halide, perchlorate, fluoborate, acetate, bisul-
fate and sulfate;
7

3,869,454

R₅ represents a member selected from the group consisting of hydrogen and

\[ O - R_{15} \]

wherein W represents a member selected from the group consisting of oxygen and sulfur, and R₄ represents a member selected from the group consisting of amino and lower alkyl having 1-4 carbon atoms, R₆ and R₇ each independently represent a member selected from the group consisting of hydrogen, lower alkyl having 1-4 carbon atoms and methoxy, provided that R₇ represents hydrogen when R', R₁ and R₃ represent hydrogen, R₈ and R₁₀, together with the carbon and nitrogen atoms to which they are attached, represent a member selected from the group consisting of a saturated heterocycle containing 5 ring atoms, a saturated heterocycle containing 6 ring atoms, an unsaturated heterocycle containing 6 ring atoms, in which case R₆ represents hydrogen and R₁₀ represents a member selected from the group consisting of hydrogen and lower alkyl having 1-4 carbon atoms;

Or R₄ and R₁₁, together with the nitrogen atoms to which they are attached, represent a member selected from the group consisting of a saturated heterocycle containing 5 ring atoms, an unsaturated heterocycle containing 5 ring atoms, a saturated heterocycle containing 6 ring atoms, an unsaturated heterocycle containing 6 ring atoms, in which case R₄ represents hydrogen and R₁₀ represents a member selected from the group consisting of hydrogen, lower alkyl having 1-4 carbon atoms and acyl having 2 to 5 carbon atoms.

These novel compounds according to the present invention are obtained by known processes, including condensation of a hydrazone of the general formula

\[ A = N - \text{NH₂} \]

wherein A has the signification indicated above, with a coupler corresponding to one of the following formulæ:

\[ \text{or} \]

where Y' designates a residue -NHR', or

and radicals R₁ to R₁₁, R', R₁₂ and Z have the signification indicated above. This condensation being performed in the presence of an oxidizing agent which can be hydrogen peroxide, an alkaline persulfate, an alkaline chloride, potassium ferricyanide or ferric chloride, at a temperature between 15 and 70°C, either in an alkaline medium or an acid medium, in case it is desired to obtain a compound with a quaternary ammonium group. The acid used can be that corresponding to the desired salt, or a different acid, in which case the condensation is followed by an addition to the reaction medium of a salt of the acid corresponding to the desired diazamocyanine salt that is more soluble in water than said diazamocyanine salt, which is then isolated by filtering. This method of preparation has been generally described by S. Hunig in "Angewandte Chemie," International Edition, Volume 7, pages 335-344 (1968), the disclosure of which is hereby incorporated by reference.

The following examples are intended to illustrate various aspects of the present invention. Unless otherwise indicated, all parts and percentages are by weight and all temperatures used herein are expressed in degrees centigrade.

**EXAMPLE 1**

3-methyl 2,3-dihydro 2'-azino benzothiazole 3'-amino 6'-methyl 1'-oxy 1',4'-dihydro benzene having the formula as indicated below is prepared as follows:

To a solution of 1.80 g of 3-methyl benzothiazolone hydrazone (0.01 mole) in 100 cc of 50% alcohol, a solution of 1.60 g of 3-amino 6-methyl phenol (0.01 mole) in 50 cc of 50% alcohol and 5 cc of ammonia at...
22°Be are added successively. The mixture is main tained at 30°C with stirring, then there is introduced a solution of 2.28 g of ammonium persulfate in 20 cc of 50% alcohol. Stirring is continued for 30 minutes, then the precipitate obtained is drained, washed with water and dried on phosphoric anhydride.

The dye is in the form of a reddish brown solid with a melting point above 260°.

Molecular weight found by potentiometric determination in glacial acetic acid with HClO 4, N/10 = 297, (the theoretical value is 298).

**EXAMPLE 2**

3-methyl 2,3-dihydro 2:4'-azino benzothiazole 2',6'-dimethyl 1'-oxo 1',4'-dihydro benzene having the formula below is prepared as follows:

In a manner similar to that of Example 1, but using 2,6-dimethyl phenol for the 2-amino-6-methyl phenol, the above-indicated dye is obtained in form of a bright red solid with a melting point of 236°. Molecular weight was calculated in a similar manner as Example 1 and found by potentiometric determination to be 300 (theory: 297).

**EXAMPLE 3**

Preparation of 3-methyl 2,3-dihydro 2:4'-azino benzothiazole 3'-acetamino 6'-methyl 1'-oxo 1',4'-dihydro benzene having the formula below is prepared as follows:

In a manner identical to that of Example 1, but using 3-acetamino-6-methyl phenol a reddish orange product is obtained with a melting point of 236°. Similarly, molecular weight was calculated by potentiometric determination and found to be 350 (theory: 340).

**EXAMPLE 4**

Preparation of 3-methyl 2,3-dihydro 2:4'-azino benzothiazole 3'-amino 2',6'-dimethyl 1'-oxo 1',4'-dihydro benzene having the formula below is prepared as follows:

In a manner identical to that of Example 1, but using 3-amino-2,6-dimethyl phenol a brown product is obtained with a melting point of 250°.

Molecular weight was determined by potentiometric determination and found to be 321 (theory: 312).

**EXAMPLE 5**

3-phenyl 4-methyl 2,3-dihydro 2:4'-azino thiazole 1',4'-dihydro 1'-oxo 2'-naphthanilide having the formula below was prepared as described by S. Huenig in “Liebigs Annalen der Chemie,” Vol. 47, p. 77, the disclosure of which is hereby incorporated by reference.

A red product is obtained with a melting point of 238°.

**EXAMPLE 6**

3,4-diphenyl 2,3-dihydro 2:4'-azino thiazole 1',4'-dihydro 1'-oxo 2'-naphthanilide having the following formula:

is prepared as described in Example 5, but using 3,4-diphenyl 2,3-dihydrothioazole.

A red product is obtained with a melting point of 240°.

**EXAMPLE 7**

2[(1-dimethylamino-phenyl (4) azo)-3 methyl benzothiazolium perchlorate having the following formula:
is prepared by the method described by S. Huenig in "Liebigs Annalen der Chemie," Vol. 628, p. 88, the disclosure of which is hereby incorporated by reference.

A product with green glints is obtained with a melting point of 230°.

EXAMPLE 8
1,3-dimethyl-2[(1-dimethylamino phenyl (4)) azo]imidazolium perchloate having the following formula:

![Formula Image]

is prepared by the method described by S. Huenig in "Liebigs Annalen der Chemie," Vol. 628, p. 90, the disclosure of which is hereby incorporated by reference.

A product with green glints is obtained with a melting point of 242°.

EXAMPLE 9
2[(1,3-diamino 6-methyl-phenyl (4)) azo]-3 methyl benzothiazolium iodide having the below formula, is prepared as follows:

![Formula Image]

1.80 g of N-methyl benzothiazolone hydrazone are dissolved in 200 cc of 50% methanol. A solution of 1.74 g of 1-phenyl-3-methyl-5-pyrazolone in 50 cc of 50% methanol are added and then a solution of 14.5 g of potassium ferricyanide in a mixture of 100 cc of 50% methanol and 10 cc of 25% ammonia are introduced with stirring. The reaction mixture is stirred for a half hour, then 300 cc of water are added. The precipitate that results is drained, washed with water and dried on phosphoric anhydride. The dye obtained is in the form of a reddish orange solid with a melting point of 262°.

EXAMPLE 10
2[(1,3-diamino 2,6-dimethyl phenyl (4)) azo]-3 methyl benzothiazolium iodide having the below formula

![Formula Image]

is prepared in a manner identical with that of Example 9, except that 1,3-diamino 2,6-dimethyl phenol is employed.

The dye is isolated in the form of a reddish violet solid with a melting point of 170° (decomposition).

EXAMPLE 11
3-methyl 2,3-dihydro 2′:4′-azino benzothiazole 1′-phenyl 3′-methyl 4′-yldene 5′-pyrazolone of the below formula is prepared as follows:

![Formula Image]

1.80 g of N-methyl benzothiazolone hydrazone are dissolved in 160 cc of normal hydrochloric acid containing 10 mg of ferrous sulfate. 1.22 g of metatolyene diamine are added and thereafter 2.5 cc of 30% hydrogen peroxide are added with stirring. The reaction mixture is stirred for a half hour at 30°C, then 10 cc of formic acid are added. The reaction mixture is next heated to 70°C, it is filtered and 2.2 g of potassium iodide are added to the filtrate. After cooling the precipitate is drained, washed with water and dried on phosphoric anhydride.

The dye is obtained in the form of a reddish violet solid with a melting point of 180° (decomposition).

EXAMPLE 12
1,3-dimethyl 2,3-dihydro 2′:4′-azino benzimidazole 1′-phenyl 3′-methyl 4′-yldene 5′-pyrazolone of the below formula:

![Formula Image]

is prepared in a manner identical with that of Example 11, except that 1,3-dimethyl 2,3-dihydro benzimidazole hydrazone is employed.
The dye is isolated in the form of a reddish orange product with a melting point of 268°.

EXAMPLE 13
1,2-dimethyl 2,3-dihydro 2:4'-azino indazole 1'-phenyl 3'-methyl 4'-pyrazolone of the below formula

is prepared in a manner similar to that of Example 11. The dye is obtained in the form of a brownish orange product with a melting point of 264°.

Molecular weight calculated by potentiometric determination was found to be 348 (theory: 346).

EXAMPLE 14
4-methyl 3-phenyl 2,3-dihydro 2:4'-azino thiazole 1'-phenyl 3'-methyl 4'-ylidene 5'-pyrazolone of the below formula

is prepared in a manner similar to that described in Example 11. An orange product is obtained with a melting point of 232°.

EXAMPLE 15
1-methyl 1,4-dihydro 4:4'-azino pyridine 1',4'-dihydro 1'-oxo benzene of the below formula:

is prepared in a manner as described by S. Huenig in "Liebigs Annalen der Chemie," Vol. 636, p. 27, the disclosure of which is hereby incorporated by reference. A dye is obtained in the form of a deep violet solid with a melting point of 213°.

EXAMPLE 16
1-methyl 1,4-dihydro 4,4'-azino pyridine 1',4'-dihydro 1'-oxo naphthalene of the below formula:

is prepared in a manner identical with that described in Example 17. The dye is obtained in the form of a brown solid with green glints having a melting point of 184°. Molecular weight found: 324. Molecular weight calculated (theoretical): 323.

EXAMPLE 19
3-methyl 2,3-dihydro 2:7'-aminobenzotriazole 6'-oxo 6',7'-dihydro benzomorpholine of the below formula:
is prepared in a manner identical with that described in Example 17. The dye is obtained in the form of a brown solid with a melting point of 195°C.

**EXAMPLE 20**

7'-6'-hydroxy benzomorpholine) 2-azo 3-methyl benzothiazolium chloride of the below formula, is prepared as follows:

2.52 g (0.01 mole) of N-methylbenzothiazolone hydrazide dihydrochloride and 1.51 g (0.01 mole) of 6-hydroxy benzomorpholine are dissolved in 200 cc of 1 N HCl, then, over a period of 45 minutes, 26 cc of 28° FeCl₃ dissolved in 24 cc of water is added. The mixture takes on a violet shade and a precipitate appears. The reaction mixture is allowed to react for 15 minutes, then filtered and the product dried under vacuum on phosphoric anhydride. The chloride thus obtained is purified by dissolving in dimethylformamide and reprecipitation with water. Melting point: 225°C (decomposition).

Analysis:
- C%: 48.66 - 48.66 (49.3 theoretical)
- H%: 3.87 - 3.99 (4.62 theoretical)
- N%: 14.35 - 15.51 (14.12 theoretical)

**EXAMPLE 21**

7'-6'-hydroxy benzomorpholine) 2-azo 3-methyl benzothiazolium perchlorate of the below formula, is obtained by dissolving of the chloride prepared in Example 20 in a suitable quantity of acetic acid and reprecipitation by sodium perchlorate.

1.33 g (0.005 mole) of 3,4-diphenyl thiazolone benzene sulfonylhydrazine and 0.75 g (0.005 mole) of 6-hydroxy benzomorpholine are dissolved in 50 cc of crystallizable acetic acid. 2.28 g (0.001 mole) of ammonium persulfate dissolved in 10 cc of water are added in 30 minutes and an intense violet coloring appears. After stirring the reaction mixture for 30 minutes, 2 g of sodium perchlorate dissolved in 10 cc of water are added. The reaction mixture is filtered, washed with water and dried under a vacuum on phosphoric anhydride. The product is purified by dissolving in a sufficient quantity of dichloethane and precipitation by carbon tetrachloride, there being obtained crystals with green glints with a melting point of 170°C.
Analysis:  
C%: 52.57 – 52.60 (52.75 theoretical)  
H%: 4.38 – 4.10 (3.82 theoretical)  
N%: 10.05 – 10.29 (10.7 theoretical)  

Determination by water (Karl Fisher): 1.5%  

EXAMPLE 24  

7'-4(6'-hydroxy benzomorpholine)-2-azo 1,3-dimethyl benzimidazolium perchlorate of the below formula, is prepared as follows:  

\[
\text{CH}_3 \text{N} \quad \text{O} \\
\text{ClO}_4^-
\]

10 g (0.04 mole) of N,N'-dimethyl benzimidazolone hydrazone dihydrochloride and 6.04 g (0.04 mole) of 6-hydroxy benzomorpholine are dissolved in 250 cc of acetic acid. 30 g of sodium acetate dissolved in 100 cc of acetic acid are added and then, in about 30 minutes, 18.24 g (0.08 mole) of ammonium persulfate dissolved in 100 cc of water are added. The mixture is allowed to react for 30 minutes, then the inorganic salts are separated by filtering and the product is precipitated by addition of 20 g of sodium perchlorate dissolved in 300 cc of water. 9 g of the product are collected, corresponding to a yield of 70%, which is purified by extraction with methanol and concentration. The melting point was found to be 240°C.  

Analysis:  
C\(_6\)H\(_8\)N\(_2\)O\(_2\) \cdot ClO\(_4\)  
C%: 48.6 (48.2 theoretical)  
H%: 4.6 (4.2 theoretical)  

The following examples relate to another embodiment of the present invention wherein the dyes produced in the preceding examples are used in hair-setting lotions as hereinbefore described.  

EXAMPLE 25  

The following hair-setting lotion is prepared  

Dye of Example 7 0.100 g  
Vinyl acetate-crotonic acid copolymer (vinyl acetate – 90 %, crotonic acid – 10 %, molecular weight 45,000 – 50,000) 3 g  
Ethyl alcohol, 96° titer 50 cc  
Triethanolamine, q.s.p. pH 7  
Water, q.s.p. 100 cc  

This hair-setting lotion when applied to hair dyed brown, imparts thereto a purplish brown shade.  

EXAMPLE 26  

The following hair-setting lotion is prepared:  

Dye of Example 7 0.03 g  
Vinyl pyrrolidone-vinyl acetate copolymer (vinyl pyrrolidone - 70 %, vinyl acetate - 30 %, molecular weight 35,000 – 45,000) 2 g  
Ethyl alcohol, 96° titer 50 cc  
200 volume hydrogen peroxide 5 g  
Orthophosphoric acid, q.s.p. pH 3  
Water, q.s.p. 100 cc  

This hair-setting lotion when applied to hair dyed deep blond, imparts thereto a luminous ash glint.  

EXAMPLE 27  

The following dyeing composition is prepared:  

Dye of Example 7 0.0012 g  
Vinyl pyrrolidone-vinyl acetate copolymer (vinyl pyrrolidone - 70 %, vinyl acetate - 30 %, molecular weight 35,000 – 45,000) 2 g  
Ethyl alcohol, 96° titer 50 cc  
200 volume hydrogen peroxide 5 g  
Orthophosphoric acid, q.s.p. pH 3  
Water, q.s.p. 100 cc  

This hair-setting lotion is applied at ambient temperature to naturally light brown hair. After setting and drying, the hair is lightly brightened and imparts thereto a pearly glint.  

EXAMPLE 28  

The following composition is prepared:  

Dye of Example 7 0.0015 g  
Ethyl alcohol, 96° titer 50 cc  
200 volume hydrogen peroxide 5 g  
Orthophosphoric acid, q.s.p. pH 3  
Water, q.s.p. 100 cc  

This composition is applied to naturally dark blond hair. After setting and drying the hair is lightly brightened up and the lotion imparts thereto an ash rose glint.  

EXAMPLE 29  

The following dyeing composition is prepared  

Dye of Example 7 0.0006 g  
Dye of Example 8 0.0006 g  
Vinyl acetate-crotonic acid copolymer (vinyl acetate - 90 %, crotonic acid - 10 %, molecular weight 45,000 – 50,000) 2 g  
Ethyl alcohol, 96° titer 55 cc  
200 volume hydrogen peroxide 5 g  
Orthophosphoric acid, q.s.p. pH 3  
Water, q.s.p. 100 cc  

This lotion is applied to natural blond hair. After setting and drying, the hair is brightened and presents an ash pearly blond shade.  

EXAMPLE 30  

The following dyeing composition suitable for packaging in an aerosol container is prepared:  

Dye of Example 4 0.03 g  
Dye of Example 1 0.1 g  
Vinyl pyrrolidone-vinyl acetate copolymer (vinyl pyrrolidone - 60 %, vinyl acetate - 40 %, molecular weight 45,000 – 60,000) 3 g  
Ethyl alcohol, 96° titer, q.s.p. 100 cc
This composition, packaged in an aerosol container with dichlorodifluoromethane as the propellant and sprayed in the form of a lacquer gives natural blond hair luminous golden glints.

**EXAMPLE 31**
The following hair-setting lotion is prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye of Example 11</td>
<td>0.005 g</td>
</tr>
<tr>
<td>Dye of Example 1</td>
<td>0.01 g</td>
</tr>
<tr>
<td>Dye of Example 8</td>
<td>0.001 g</td>
</tr>
<tr>
<td>Vinyl pyrrolidone-vinyl acetate copolymer</td>
<td>2 g</td>
</tr>
<tr>
<td>Ethyl alcohol, 96° titer</td>
<td>50 cc</td>
</tr>
<tr>
<td>Triethanolamine, q.s.p.</td>
<td>pH 7</td>
</tr>
<tr>
<td>Water, q.s.p.</td>
<td>100 cc</td>
</tr>
</tbody>
</table>

This hair-setting lotion when applied to freshly bleached hair, imparts thereto a light silvery shade.

**EXAMPLE 32**
The following dyeing composition is prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye of Example 17</td>
<td>0.096 g</td>
</tr>
<tr>
<td>Butylcellulose</td>
<td>8 g</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>8 g</td>
</tr>
<tr>
<td>Alkylphenol polyethoxys ether sold under the name “Remcopal 334” by the Gerland company</td>
<td>22 g</td>
</tr>
<tr>
<td>Alkylphenol polyethoxys ether sold under the name “Remcopal 349” by the Gerland company</td>
<td>22 g</td>
</tr>
<tr>
<td>Ammonia at 22°C</td>
<td>8 g</td>
</tr>
<tr>
<td>Water, q.s.p.</td>
<td>100 g</td>
</tr>
</tbody>
</table>

20 g of 20 volume hydrogen peroxide is added to 20 g of the solution thus prepared and the gel thus obtained which, applied to ambient temperatures to bleached hair for 10 minutes, imparts to the hair a beige pearly shade.

**EXAMPLE 33**
The following dyeing composition is prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye of Example 17</td>
<td>0.2 g</td>
</tr>
<tr>
<td>Butylcellulose</td>
<td>8 g</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>8 g</td>
</tr>
<tr>
<td>Alkylphenol polyethoxys ether sold under the name “Remcopal 334” by the Gerland company</td>
<td>22 g</td>
</tr>
<tr>
<td>Alkylphenol polyethoxys ether sold under the name “Remcopal 349” by the Gerland company</td>
<td>22 g</td>
</tr>
<tr>
<td>Ammonia at 22°C</td>
<td>10 g</td>
</tr>
<tr>
<td>Water, q.s.p.</td>
<td>100 g</td>
</tr>
</tbody>
</table>

20 g of water are added to 20 g of the solution thus prepared. A gel is obtained which, applied to brown hair at ambient temperature for 15 minutes, imparts to the hair, after rinsing, a dark auburn brown shade.

**EXAMPLE 34**
The following dyeing composition is prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye of Example 8</td>
<td>0.050 g</td>
</tr>
<tr>
<td>Butylcellulose</td>
<td>8 g</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>8 g</td>
</tr>
<tr>
<td>Alkylphenol polyethoxys ether sold under the name “Remcopal 334” by the Gerland company</td>
<td>22 g</td>
</tr>
<tr>
<td>Alkylphenol polyethoxys ether sold under the name “Remcopal 349” by the Gerland company</td>
<td>22 g</td>
</tr>
<tr>
<td>Water, q.s.p.</td>
<td>100 g</td>
</tr>
</tbody>
</table>

20 g of water are added to 20 g of the solution thus prepared. A gel is obtained which, applied at ambient temperature for 10 minutes to previously bleached hair, imparts to the hair an iridescent blond shade.

**EXAMPLE 35**
The following hair-setting lotion is prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye of Example 20</td>
<td>0.010 g</td>
</tr>
<tr>
<td>Vinyl pyrrolidone-vinyl acetate copolymer</td>
<td>2.0 g</td>
</tr>
<tr>
<td>Ethyl alcohol, 96° titer</td>
<td>50 cc</td>
</tr>
<tr>
<td>Triethanolamine, q.s.p.</td>
<td>pH 7</td>
</tr>
<tr>
<td>Water, q.s.p.</td>
<td>100 cc</td>
</tr>
</tbody>
</table>

This hair-setting lotion when applied to hair dyed blond, imparts thereto a golden glint.

**EXAMPLE 36**
The following hair-setting composition is prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye of Example 22</td>
<td>0.012 g</td>
</tr>
<tr>
<td>Vinyl pyrrolidone-vinyl acetate copolymer</td>
<td>2.0 g</td>
</tr>
<tr>
<td>Ethyl alcohol, 96° titer</td>
<td>50 cc</td>
</tr>
<tr>
<td>Triethanolamine, q.s.p.</td>
<td>pH 7</td>
</tr>
<tr>
<td>Water, q.s.p.</td>
<td>100 g</td>
</tr>
</tbody>
</table>

This hair-setting lotion when applied to bleached hair, imparts thereto a particularly luminous golden pink blond shade.

**EXAMPLE 37**
The following hair-setting lotion is prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye of Example 24</td>
<td>0.010 g</td>
</tr>
<tr>
<td>Vinyl pyrrolidone-vinyl acetate copolymer</td>
<td>2.0 g</td>
</tr>
<tr>
<td>Ethyl alcohol, 96° titer</td>
<td>50 cc</td>
</tr>
<tr>
<td>Triethanolamine, q.s.p.</td>
<td>pH 7</td>
</tr>
<tr>
<td>Water, q.s.p.</td>
<td>100 cc</td>
</tr>
</tbody>
</table>

This hair-setting lotion when applied to hair dyed golden blond, imparts thereto a luminous and aesthetic pearl glint.

**EXAMPLE 38**
The following hair-setting lotion is prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye of Example 23</td>
<td>0.015 g</td>
</tr>
<tr>
<td>Vinyl pyrrolidone-vinyl acetate copolymer</td>
<td>2.0 g</td>
</tr>
<tr>
<td>Ethyl alcohol, 96° titer</td>
<td>50 cc</td>
</tr>
<tr>
<td>Triethanolamine, q.s.p.</td>
<td>pH 8</td>
</tr>
<tr>
<td>Water, q.s.p.</td>
<td>100 cc</td>
</tr>
</tbody>
</table>

This hair-setting lotion when applied to bleached hair, imparts thereto a very luminous light pink blond shade.

**EXAMPLE 39**
The following hair-setting lotion is prepared:
This hair-setting lotion when applied to hair dyed dark blond, imparts thereto a luminous pearl ash glint.

**EXAMPLE 40**

The following hair-setting lotion is prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye of Example 22</td>
<td>0.010 g</td>
</tr>
<tr>
<td>N-{(4'-amino 2'-methoxy 3',5'-dimethyl)phenyl} 2,5-dimethyl benzoquinonimine</td>
<td>0.012 g</td>
</tr>
<tr>
<td>Ethyl alcohol, 96° titer</td>
<td>50 cc</td>
</tr>
<tr>
<td>Water, q.s.p.</td>
<td>100 cc</td>
</tr>
</tbody>
</table>

This hair-setting lotion, when applied to light blond hair, imparts thereto a pearl ash shade.

**EXAMPLE 41**

The following dyeing composition is prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye of Example 24</td>
<td>0.005 g</td>
</tr>
<tr>
<td>N-{(4'-hydroxyphenyl)-3-aminobenzquinonimine}</td>
<td>0.0025 g</td>
</tr>
<tr>
<td>N-{(4'-amino 2'-methoxy 3',5'-dimethyl)phenyl} 2,5-dimethyl benzoquinonimine</td>
<td>0.001 g</td>
</tr>
<tr>
<td>Vinyl pyrrolidone-vinyl acetate copolymer</td>
<td>2.0 g</td>
</tr>
<tr>
<td>Triethanolamine, q.s.p.</td>
<td>pH 7</td>
</tr>
<tr>
<td>Water, q.s.p.</td>
<td>100 cc</td>
</tr>
</tbody>
</table>

This dye composition when applied to strongly bleached hair for 20 minutes at ambient temperature, imparts thereto a golden apricot shade.

**EXAMPLE 42**

The following hair-setting composition is prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye of Example 20</td>
<td>0.005 g</td>
</tr>
<tr>
<td>N-{(4'-hydroxyphosphoryl)-3-aminobenzquinonimine}</td>
<td>0.005 g</td>
</tr>
<tr>
<td>N-{(4'-amino 2'-methoxy 3',5'-dimethyl)phenyl} 2,5-dimethyl benzoquinonimine</td>
<td>0.002 g</td>
</tr>
<tr>
<td>Vinyl pyrrolidone-vinyl acetate copolymer</td>
<td>2.0 g</td>
</tr>
<tr>
<td>Triethanolamine, q.s.p.</td>
<td>pH 7</td>
</tr>
<tr>
<td>Water, q.s.p.</td>
<td>100 cc</td>
</tr>
</tbody>
</table>

This hair-setting lotion when applied to blond hair imparts thereto a pearly glint.

**EXAMPLE 43**

The following setting lotion is prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye of Example 24</td>
<td>0.006 g</td>
</tr>
<tr>
<td>Dye of Example 22</td>
<td>0.004 g</td>
</tr>
<tr>
<td>N{(4'-hydroxyphosphoryl)-3-aminobenzquinonimine}</td>
<td>0.001 g</td>
</tr>
<tr>
<td>N{(4'-amino 2'-methoxy 5'-methylphosphoryl)-3-acetamido 6-methyl benzquinonimine}</td>
<td>0.005 g</td>
</tr>
<tr>
<td>Vinyl pyrrolidone-vinyl acetate copolymer</td>
<td>2.0 g</td>
</tr>
<tr>
<td>Ethyl alcohol, 96° titer</td>
<td>50 cc</td>
</tr>
</tbody>
</table>

This hair-setting lotion when applied to hair bleached and dyed dark brown imparts thereto a luminous blush ash glint.

As used in the preceding examples, “Remcopal 334” is a nonylphenol polyethoxyether obtained by condensation of 4 moles of ethylene-oxide with 1 mole of nonylphenol, and “Remcopal 349” is a nonylphenol polyethoxyether obtained by condensation of 9 moles of ethylene-oxide with 1 mole of nonylphenol. Both are commercially available from the Gerland company.

What is claimed is:

1. A diazamocrocyanine, including the mesomorphic form thereof, having the formula

\[
\begin{align*}
&\text{Dye of Example 7} \\
&\text{Vinyl acetate-crotonic acid copolymer} \\
&\text{(vinyl acetate - 90%, crotonic acid - 10%, molecular weight: 45,000 - 50,000)} \\
&\text{Ethyl alcohol, 96° titer} \\
&\text{Benzyldiene camphor} \\
&\text{Triethanolamine, q.s.p.} \\
&\text{pH 7} \\
&\text{Continued} \\
&\text{Triethanolamine, q.s.p.} \\
&\text{Benzylidine camphor} \\
&\text{Water, q.s.p.} \\
&\text{pH 7} \\
&\text{This hair-setting lotion when applied to very light natural blond hair, imparts thereto a luminous ash pearl glint.} \\
\end{align*}
\]
wherein A is a nitrogen heterocycle selected from the group consisting of

$$R = \text{lower alkyl having 1-4 carbon atoms or phenyl;}$$

$$X = \text{a member selected from the group consisting of oxygen, sulfur, } -NR'-. \text{ where } R' \text{ is lower alkyl having 1-4 carbon atoms; } -\text{CH}=\text{CH}-;$$

$$-\text{C}==\text{N}-;$$

where \( R'' \) is hydrogen or lower alkyl having 1-4 carbon atoms; or \( -\text{C}(R'')(\text{R}''')-. \text{ where } R'' \text{ and } R''' \text{ each independently have the meaning above;}

$$Z = -\text{CH}=\text{CH}- \text{ or } -\text{NR'''}-. \text{ where } R'''' \text{ is lower alkyl having 1-4 carbon atoms}

$$R_1 \text{ is hydrogen, lower alkyl having 1-4 carbon atoms, or phenyl;}

$$R_n \text{ is hydrogen or lower alkyl having 1-4 carbon atoms, or } R_1 \text{ and } R_n \text{ when taken together with the carbon atoms to which they are attached form a benzene ring, a halogen-substituted benzene ring, a benzene ring substituted with lower alkyl having 1-4 carbon atoms, a benzene ring substituted with lower alkoxy having 1-4 carbon atoms, or a nitro-substituted benzene ring; and } B' \text{ is a member selected from the group consisting of}

where \( R_a \text{ and } R_b \text{, together with the carbon and nitrogen atoms to which they are attached, form a morpholine group and } R_a \text{ is hydrogen and } R_{11} \text{ is hydrogen or lower alkyl having 1-4 carbon atoms, or } R_a \text{ and } R_{11} \text{, together with the carbon and nitrogen atoms to which they are attached, form a morpholine group, and } R_a' \text{ is hydrogen and } R_{10} \text{ is hydrogen, lower alkyl having 1-4 carbon atoms and alkanoyl having 2 to 5 carbon atoms; and } X^- \text{ is a halide, fluororate, perchlorate, sulfate, disulfate or acetate anion.}

2. The compound of claim 1 which is selected from the group consisting of:

- 1,2-dimethyl 2,3-dihydro 3:7'-azino indazole 6'-oxo 6',7'-dihydro benzomorpholine,
- 1,3-dimethyl 1,2-dihydro 2:7'-azino benzimidazolone 6'-oxo 6',7'-dihydro benzomorpholine,
- 3-methyl 2,3-dihydro 2:7'-aminobenzothiazole 6'-oxo 6',7'-dihydro benzomorpholine,
- 7':(6'-hydroxy benzomorpholine) 2-azo 3-methyl benzothiazolium chloride,
- 7':(6'-hydroxy benzomorpholine)2-azo 3-methyl benzothiazolium perchlorate,
- 7:(6'-hydroxy benzomorpholine) 2-azo 4-methyl 3-phenyl thiazolium perchlorate,
- 7:(6'-hydroxy benzomorpholine) 2-azo 3,4-diphenyl thiazolium perchlorate, and
- 7:(6'-hydroxy benzomorpholine) 2-azo 1,3-dimethyl benzimidazolium perchlorate.

* * * * *
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,869,454 Dated March 4, 1975

Inventor(s) Gerard LANG and Andree BUGAULT

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Heading -

Under Foreign Application Priority Data

Change "France" (both occurrences) to

-- Luxembourg --

Signed and Sealed this
twenty-first Day of October 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,869,454 Dated March 4, 1975

Inventor(s) Gerard LANG and Andree BUGAUT

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Heading -

Under Foreign Application Priority Data

Change "France" (both occurrences) to

-- Luxembourg --

Signed and Sealed this
twenty-first Day of October 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks